

**MARKING FILM, RECEPTOR SHEET AND MARKING FILM FOR VEHICLES**

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**Field of Invention**

5 The present invention relates to a marking film comprising a receptor film that receives a colorant such as a toner for forming an image (an image-displaying layer) or a coloring layer, and an adhesive layer having an uneven adhesion surface.

**Background of the Invention**

10 A receptor sheet, on the front surface of which an image (an image-displaying layer) or a coloring layer can be formed by applying a toner or an ink as a colorant, is used to produce a marking film. The receptor sheet usually has a receptor film, which includes a base layer and a receptor layer comprising a thermoplastic resin film provided on the surface of the base layer. In general, an adhesive layer is provided on the back surface of the receptor film to allow the receptor sheet to be adhered to an adherent.

15 Marking films are produced by forming an image, etc. on the surface of the receptor sheet (i.e. the receptor film) with, for example, electrostatic toner printing. When the printed surface (the colorant-receptive surface of the receptor layer) should be protected, it is covered with a protective film. Protective film, such as a polymer film made of a fluoropolymer, an acrylic polymer, a phthalate polyester (e.g. polyethylene terephthalate), etc., that has  
20 transparency such that the toner (the image, etc.) is seen through the film, is generally used.

Thermoplastic resin film of the receptor layer may be formed from various resin compositions. For example, JP-A-9-507309 discloses the use of a flexible thermoplastic resin film comprising a polyurethane-acrylic copolymer latex rubber, an acrylic resin, a vinyl chloride copolymer such as a vinyl chloride-vinyl acetate copolymer, and a plasticizer as a  
25 receptor layer of a receptor film. JP-B-3080674 discloses the use of an acrylic resin, polyolefin, polyvinyl acetal, polyvinyl chloride, polyurethane, etc. as a resin material of a receptor layer or a base layer. However, a phenoxy resin has not been proposed to be used as a resin material of a receptor layer or a base layer.

JP-A 2002-19303 discloses a film for a window using a polymethyl methacrylate film which can be thermally transferred. However, conventional polymethyl methacrylate films have low flexibility and thus low followability to curved surfaces. Therefore, such films are insufficient for use as marking films to be adhered to curved surfaces such as the body surfaces of vehicles.

It is also known to form unevenness on an adhesion surface of an adhesive layer of a marking film to prevent air trapping (i.e. permit the escape of bubbles ) between the adhesive layer and an adherent, when the marking film (or the receptor film) is adhered (applied) to the adherent. Such an adhesive layer has projections and depressions surrounding the projections, and further grooves which are defined by the depressions and communicate with the atmosphere, that is, conduits are formed between the adherent surface and the adhesion surface of the adhesive layer.

The unevenness on the adhesion surface may be formed by laminating a release paper (a liner) having unevenness on a release surface onto the adhesive layer. A marking film using such an uneven release paper is disclosed in WO00/6985, US Patent No. 6,203,885, JP-A 2001-507732, JP-Utility Model-2,503,717, JP-Utility Model-2,687,198, etc. It is also known to effectively form depressions around projections by adding elastic microspheres to an adhesive layer to form projections containing the elastic microspheres on the adhesion surface. A marking film using such elastic microspheres is disclosed in JP-A-8-113768.

In the case of a marking film having an uneven adhesion surface, usually the above conduits are present between the adherent and the adhesive layer after the completion of application of the film. Therefore, when such a marking film is adhered to and used on a body surface of a vehicle such as a bus or a truck, a petroleum fuel, which overflows around a fuel-filling opening during filling, will fill the conduits due to a capillary action and spread in a relatively wide area of the adhesion surface (or the adherent surface). It is found that the fuel spread in such a way will permeate into the inside of the film through the adhesive layer and swell the film. The swelling with the fuel, in particular, diesel oil deteriorates the appearance of the marking film due to the peeling of the marking film from the adherent, or the peeling of the layers of the marking film.

None of the above patent publications suggest any improvement of a marking film for a vehicle, which is adhered to a body surface of the vehicle that uses a petroleum fuel such as diesel oil. That is, they do not disclose the selection and the use of specific resins to effectively increase properties for suppressing the above-described deterioration of the appearance of the marking film due to swelling caused with the petroleum fuel such as diesel oil. For example, the deterioration of the appearance due to swelling is remarkable when the receptor film contains polyolefin. A receptor layer containing polyurethane swells less, but in general polyurethane has low moisture resistance, and thus the edge of the marking film tends to be peeled from the adherent and turns up, when the marking film is used outside where it is exposed to wind and weather for a relatively long time (for example, six months).

### Summary of the Invention

To solve the above problems, the present invention provides a marking film comprising:

- (a) a receptor film having a colorant-receptive front surface, and a back surface opposing to said front surface,
  - (b) a colorant received on said front surface of the receptor film, and
  - (c) an adhesive layer fixedly provided on said back surface of the receptor film and comprising an adhesive that adheres said receptor film to an adherent,
- wherein said adhesive layer has projections containing said adhesive, which are formed on an adhesion surface to be adhered to said adherent, and depressions surrounding said projections, and said depressions define conduits, which communicate with the atmosphere, between the surface of said adherent and the adhesion surface of said adhesive layer when said adhesive layer is being adhered to said adherent.

Further, the receptor film comprises a receptor layer formed of a thermoplastic resin film having a surface that serves as said colorant-receptive surface, and said thermoplastic resin film comprises a resinous component containing at least one petroleum-resistant resin selected from the group consisting of polyurethane comprising polyol units derived from polycarbonate polyol, polyurethane comprising polyol units derived from polycaprolactone

polyol and phenoxy resins, or in that said receptor film is a petroleum-resistant resin film containing a copolymer comprising a least one alkyl acrylate having 1 to 8 carbon atoms in the alkyl group and methyl methacrylate.

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### **Brief Description of the Drawings**

Fig. 1 A cross-sectional view of one example of the marking film of the present invention.

### **Preferred Embodiment(s) of the Present Invention**

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In the marking film of the present invention, the receptor layer contains at least one petroleum-resistant resin selected from the group consisting of polyurethane comprising polyol units derived from polycarbonate polyol, polyurethane comprising polyol units derived from polycaprolactone polyol and phenoxy resins, or in that said receptor film is a petroleum-resistant resin film containing a copolymer comprising a least one alkyl acrylate having 1 to 8 carbon atoms in the alkyl group and methyl methacrylate. Accordingly, the marking film of the present invention can effectively prevent the swelling caused by the penetration of the petroleum fuel such as diesel oil or gasoline into the receptor layer through the adhesive layer. Therefore, the deterioration of the appearance of the marking film caused by the penetration of the fuel can be effectively prevented when the marking film is adhered to and used on the body surface of a vehicle. In addition, the petroleum-resistant resin exhibits moisture resistance, since the resin is resistant to hydrolysis. Accordingly, the marking film of the present invention can effectively suppress edge curl of the marking film when it is used outdoors where it is exposed to rain and weather.

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If the surface of the receptor film may possibly come in contact with diesel oil, it is preferable to protect the image-forming surface (the surface receiving the colorant) of the receptor film with a protective film comprising a fluoro-resin. Furthermore, it is effective to use a protective film made of a resin composition containing at least one petroleum-resistant resin selected from the above group.

The receptor film may have a base layer between the receptor layer and the adhesive layer, although it is preferable to have only the receptor layer and the adhesive layer. When the thickness of the marking film is reduced, the flexibility of the marking film as a whole can be increased so that the applicability of the marking film to an adherent having a curved surface is effectively improved.

When the receptor film includes the base layer, the base layer preferably comprises at least one petroleum-resistant resin selected from the group consisting of polyurethane comprising polyol units derived from polycarbonate polyol, polyurethane comprising polyol units derived from polycaprolactone polyol and phenoxy resins, or in that said receptor film is a petroleum-resistant resin film containing a copolymer comprising a least one alkyl acrylate having 1 to 8 carbon atoms in the alkyl group and methyl methacrylate. Thus, the base layer functions as a barrier layer and the penetration of the fuel such as diesel oil in the receptor layer can more effectively be suppressed.

According to the present invention, the film or layer containing the petroleum-resistant resin may be designed to contain substantially no polyvinyl chloride. Today, there is a demand in the market for marking film containing substantially no polyvinyl chloride, that is, so-called vinyl chloride-free marking films. The present invention can supply vinyl chloride-free marking films having good resistance to petroleum that meet such needs.

#### MARKING FILM

One preferred embodiment of the marking film of the present invention will be explained by making reference to Fig. 1.

Fig. 1 schematically shows one embodiment of the marking film of the present invention. The receptor film (1) of the marking film (100) consists of a single layer of a receptor layer made of a thermoplastic film. The thermoplastic film contains a petroleum-resistant resin, as described above. Receptor film (1) has a front surface (11) and a back surface (12), and a front surface (11) receives a colorant, that is, toner (2). Toner (2) forms an image, which is visible from the side of the outermost surface (31) of the protective film (3) through the protective film (3).

The adhesive layer (4) is fixedly provided on the back surface (12) of receptor film (1). Although not shown in Fig. 1, the projections comprising the adhesive (not shown) and the depressions (not shown) surrounding the projections are formed on the adhesion surface (41) of the adhesive layer (4), and the conduits (not shown) that are defined by the depressions and communicate with the atmosphere are formed between the adhesion surface (41) and the surface of an adherent, when the marking film is adhered to the adherent.

The adhesive of adhesive layer (4) is not limited, and is typically a pressure-sensitive adhesive comprising a self-adherent polymer. As the pressure-sensitive adhesive layer, for example, a single-layer pressure-sensitive adhesive film containing a self-adherent polymer, or a double-coated adhesive sheet having two pressure-sensitive adhesive layers is preferably used.

To adhere the protective film (3) to the receptor film (1), an additional adhesive layer (30) for the protective film is usually used. The adhesive of the adhesive layer (30) for the protective layer is not limited, and is usually a pressure-sensitive adhesive comprising a self-adherent polymer, since such an adhesive layer can follow the unevenness formed by the toner (2) on the surface (11) of the receptor film so that the protective film (3) and the receptor film (1) can be closely adhered each other while forming no air bubbles between them. The air bubbles decrease the visibility of the image, and thus it is preferable to prevent the air bubbles.

#### RECEPTOR SHEET

The receptor sheet of the present invention is a receptor film with an adhesive layer that comprises a receptor film on which a colorant such as a toner is applied, and an adhesive layer to adhere the receptor film to an adherent.

Typically, the receptor film (i) is a single layer film of the thermoplastic resin film comprising the petroleum-resistant resin, or (ii) comprises a laminate film having a receptor layer and a base layer provided between the receptor layer and the adhesive layer. Preferably, in case (ii), the base layer is also a resin film comprising the petroleum-resistant resin.

The petroleum resistance of the resin film can be evaluated as follows:

A sample of a resin film having a specific size is provided. On the surface of this sample, a drop (about 0.01 to 0.02 g) of diesel oil is dropped and kept standing at room

temperature for 10 minutes, and then the sample is visually observed. If no wrinkle is formed, the resin film is judged to have good petroleum resistance. If the resin film has high resistance to diesel oil (petroleum resistance using diesel oil), the swelling of the sheet with other petroleum fuel such as gasoline can be effectively prevented.

5           The petroleum resistance of a receptor sheet (having the adhesive layer) can be evaluated as follows:

10           A sample of a receptor sheet having a specific size is adhered to a test adherent, for example, a stoved melamine-coated plate. In this step, conduits communicating with the atmosphere are formed between the surface of the adherent and the adhesive layer. A part of the sample adhered to the adherent is dipped in diesel oil at room temperature for 8 hours, and then removed from the diesel oil and dried in the shade (without direct light) at room temperature for 16 hours. The dry sample is visually observed. If no wrinkle is formed, no peeling of the sheet from the adherent or no delamination of the layers (between the receptor film and the adhesive layer, etc.) are found, the receptor sheet is judged to have good petroleum resistance. The petroleum resistance of a marking film can be evaluated in the same manner as above.

15           In general, the moisture-resistance of a resin film is evaluated as follows:

20           A resin film is adhered to a melamine-coated plate with an adhesive to obtain a sample. The sample is placed in an oven conditioned at 65°C, 95%RH for one week. Then, the edge of the film is checked to determine whether it is turned up or not. If no edge is turned up under such conditions, the film is judged to have good moisture-resistance. The adhesive used to adhere the resin film to the melamine-coated plate is typically a pressure-sensitive acrylic adhesive. Alternatively, an adhesive, that is actually used to adhere a marking film to an adherent may also be used. The moisture resistance of a marking film can be evaluated in the same manner as above.

25           Polyurethane used as a petroleum-resistant resin is a polymer obtained by polymerizing a raw material containing the above polyol (polycarbonate polyol and/or polycaprolactone polyol) and a diisocyanate. The raw material may contain a short-chain diol such as neopentyl glycol, ethylene glycol, propylene glycol, etc. as a chain extender.

Examples of the diisocyanate include isophorone diisocyanate (IPDI), diphenylmethane diisocyanate (MDI), hydrogenated MDI, 1,6-hexanediol diisocyanate, tolylene diisocyanate (TDI), tetramethylxylylene diisocyanate (TMXDI), etc. The raw material may contain one or more polyols and one or more diisocyanates.

5           The chemical structure of the diisocyanate in the raw material, and a ratio of the short-chain diol, which is optionally a polyol are selected so that the properties of the thermoplastic resin film containing the polyurethane (e.g. a glass transition temperature, a complex dynamic viscosity and a Vicat softening point) fall within optimum ranges.

10           The glass transition temperature of the thermoplastic resin film of the receptor layer is usually from 0 to 100°C. When the glass transition temperature of the receptor layer is too high, the toner-transferability of the receptor layer deteriorates so that a clear image may not be formed. In addition, when the glass transition temperature is too high, the flexibility of the marking film as a whole tends to decrease. When the glass transition temperature is less than 0°C, petroleum resistance may deteriorate. Furthermore, the glass transition temperature of  
15           the receptor layer is preferably 0°C or higher to effectively decrease the room temperature tack of the colorant-receptive surface. When the receptor layer has such a glass transition temperature, the sticking of the marking film precursors prior to the covering with the protective film, or the receptor sheets can be effectively prevented. Accordingly, the marking film precursor or the receptor sheet can be easily unwound from a roll after it is stored in a  
20           rolled form.

          The glass transition temperature of the receptor layer is preferably from 10 to 90°C, more preferably from 20 to 80°C, to effectively increase the above effects in good balance, that is, the improvements of petroleum resistance and the toner-transfer properties, the decrease of the room temperature tack, and the increase of the film flexibility.

25           The glass transition temperature (T<sub>g</sub>) of the thermoplastic resin film of the receptor layer, etc. is measured by providing a film having a thickness of about 10 μm (usually 8 to 20 μm) as a sample and setting this sample on DSC (differential scanning calorimeter). In the measurement, the temperature is raised from -50°C to 120°C (first scanning), and then a glass



transition temperature is read from an inflection point corresponding to a secondary transition point in the first scanning.

Besides the glass transition temperature, one property of the thermoplastic resin film to be noted is a Vicat softening point of the thermoplastic resin film, which is measured using a viscoelastic spectrometer at 25°C. The Vicat softening point of the thermoplastic resin film is usually from 30 to 95°C, preferably from 40 to 93°C. When the Vicat softening point is too high, it may be difficult to transfer the toner to the resin film. When Vicat softening point is too low, the mechanical strength of the resin film decreases so that the durability of the marking film tends to deteriorate.

The Vicat softening point is a softening point measured according to Japan Industrial Standards (JIS) K 7206 by raising a temperature of a sample at a constant rate while applying a specific load to a needle-shape penetrator, which is maintained perpendicular to the sample (the thermoplastic resin film), and measuring a temperature at which the penetrator penetrates in the sample by 1 mm.

The particularly preferable polyurethane is one having polyol units derived from polycarbonate polyol in the molecule (polycarbonate polyurethane). The polycarbonate polyurethane has good weather resistance in addition to the moisture resistance, and thus effectively prevents the deterioration or coloring of a film comprising the same. The coloring of the protective film or the receptor film induces the discoloration of the image. Therefore, the receptor film and protective film that are less colored are advantageous as elements of the marking film used outdoors, in particular, the marking film for vehicles.

The number of carbon atoms of an alkylene group in the polyol backbone is preferably from 5 to 7. When the number of carbon atoms exceeds 7, the petroleum resistance of the thermoplastic resin film may deteriorate. When the number of carbon atoms is less than 5, the thermal transfer properties of the toner may deteriorate.

The molecular weight of the polyurethane is not limited, and its weight average molecular weight is usually from 20,000 to 1,000,000.

Phenoxy resins also have high petroleum resistance and moisture resistance. This is because the phenoxy resin has repeating units derived from bisphenol in the molecule.

Phenoxy resins, such as those conventionally used for paints can be used. Specific examples of commercially available phenoxy resins include "YP 50S" (trade name) available from TOTO Chemical Co., Ltd., "PKHH" (trademark) available from Phenoxy Specialties, etc. The molecular weight of the phenoxy resin is not limited insofar as it has sufficient toughness, and a weight average molecular weight usually from 20,000 to 1,000,000.

The phenoxy resin is advantageous for increasing the toughness of the receptor film since it has higher strength at break than polyurethane. The increase of the toughness of the receptor film can prevent the breakage of the marking film when the marking film is peeled for renewal and effectively decrease the workload for peeling.

When the phenoxy resin is used, it is preferably used in combination with polyurethane, since the flexibility and toughness of the receptor film can be easily increased with good balance. In such a case, the weight percentage of polyurethane in the mixture with the phenoxy resin is usually at least 60%, preferably at least 65%, more preferably at least 70%. Polyurethanes to be used in combination with the phenoxy resin are typically polycarbonate polyurethane or polycaprolactone polyurethane. When the percentage of polyurethane is 70% or less, other polyurethanes may be used.

Copolymers comprising at least one alkyl acrylate having 1 to 8 carbon atoms in the alkyl group as a soft component, and methyl methacrylate as a hard component may also be used. Such an alkyl acrylate decreases the glass transition temperature of the copolymer. The copolymer may further comprise at least one other comonomer such as methacrylates (other than methyl methacrylate), styrene, etc. The copolymer usually has a glass transition temperature of 0 to 100°C, preferably 20 to 90°C, more preferably 30 to 80°C. The amount of the alkyl acrylate is preferably at least 20% by weight based on the weight of the copolymer, but is not limited to this range.

Among the copolymers, one comprising butyl acrylate and methyl methacrylate is particularly preferred. When the acrylic copolymer is used as a petroleum-resistant resin, the receptor film is a single layer film.

The resin component constituting the receptor layer (and the base layer) may contain other resin insofar as the effects of the present invention are not impaired. One example of

the other resin is an acrylic resin. The acrylic resin is a polymer prepared by polymerizing a (meth)acrylic monomer mixture. The (meth)acrylic monomer mixture usually contains a (meth)acrylate having 1 to 10 carbon atoms in an alkyl group and other copolymerizable monomer. The other copolymerizable monomer is preferably a hydrophilic monomer such as a hydroxy(meth)acrylate, an alkylene glycol diacrylate, acrylic acid, methacrylic acid, etc. to increase the petroleum resistance. The acrylic resin can be prepared by polymerizing such a monomer mixture by a conventional polymerization method such as solution polymerization. The ratio of the monomers is suitably selected so that the glass transition temperature and other properties of the thermoplastic resin film are in optimum ranges. The molecular weight of the acrylic resin is not limited, and its weight average molecular weight is usually from 20,000 to 1,000,000.

The amount of the petroleum-resistant resin in the entire resin components contained in the thermoplastic resin film used as the receptor layer or the base layer is usually at least 70% by weight. To further increase the petroleum resistance of the film, the amount of the petroleum-resistant resin in the total resin components is preferably at least 80% by weight, particularly preferably at least 90% by weight.

The receptor sheet may be prepared as follows:

The thermoplastic resin film forming the receptor layer can be prepared by a conventional film-forming method. For example, a paint comprising the resin component is applied on a release surface of a liner and solidified to form the thermoplastic resin film. As an application apparatus, a conventional coater such as a bar coater, a knife coater, a roll coater, a die coater, etc. may be used. The solidification includes drying in the case of a paint containing a volatile solvent, cooling of a molten resin component, etc. Alternatively, the thermoplastic resin film can be formed by a melt extrusion method.

When the receptor sheet comprises the base layer and the receptor layer, it may be produced as follows although the production method is not limited thereto:

Firstly, the receptor layer is formed on a liner, and then a coating containing the resin component for the base layer is applied on the receptor layer with the liner and solidified. Thereby, the receptor film comprising the film laminate is obtained. Another layer such as a

primer layer or an adhesive layer may be provided between the receptor layer and the adhesive layer so long as the effects of the present invention are not impaired.

Then, the adhesive layer is applied to the back surface of the receptor film, which is produced as described above.

5           The adhesive layer is formed by applying a coating liquid containing the adhesive to a release surface of a liner and dried to obtain the adhesive layer with the liner, and then the adhesive layer with the liner is laminated on and adhered to the receptor film. Thereby, the receptor sheet of the present invention is finished.

10           The thickness of the receptor film as a whole is typically from 20 to 150  $\mu\text{m}$ , preferably from 30 to 100  $\mu\text{m}$ . When this thickness is too small, the mechanical strength of the film decreases and therefore the receptor sheet may be broken when the marking film is peeled from the adherent after it is adhered to the adherent. When this thickness is too large, the flexibility of the marking film including the receptor sheet may decrease.

#### ADHESIVE SHEET

15           As the adhesive sheet for adhering the marking film (or the receptor film) to the adherent, the uneven adhesive layer as described above is formed. To form the uneven adhesive layer, any of the methods disclosed in the prior art publications cited above can be used. One example of such methods is explained below:

20           Firstly, a liner having a release surface with a specific structure is provided. On the release surface of the liner, a coating containing a self-adherent polymer (an adhesive composition for forming the adhesive layer of the adhesive sheet) is applied and dried to form an adhesive layer. Thereby, the structure (negative) of the liner is transferred to the surface of the adhesive layer that is in contact with the liner (this surface forming the adhesion surface of the adhesive sheet), and thus the structured adhesion surface having the specific structure  
25           (positive) thereon is formed. The structure on the adhesion surface is designed so that it includes grooves that can form the conduits when the projections are in contact with the adherent.

          Such grooves of the adhesive layer may be provided on the adhesion surface so that grooves having a specific shape are arranged in a regular pattern, or the grooves having

irregular shapes are arranged irregularly, so long as the remaining of bubbles can be prevented when the marking film is used. When a plurality of grooves are arranged substantially in parallel, the distance between the grooves is preferably from 10 to 2,000  $\mu\text{m}$ . The depth of the groove (a distance from the adhesion surface to the bottom of the groove in the direction toward the receptor film) is usually from 10 to 100  $\mu\text{m}$ . The shape of the groove is not limited so long as the effects of the present invention are not impaired. For example, a cross-section of the groove vertical to the adhesion surface may be a rectangle (including a trapezoid), a semicircle, a semiellipse, etc.

The liner is usually made of a paper sheet or a plastic film. The paper liner is generally prepared by laminating a releasing coat (a release layer) such as a polyethylene coat, a silicone coat, etc. on the surface of the paper sheet. When the silicone release coat is laminated, usually an undercoat such as a clay coat, a polyethylene coat, etc. is laminated, and then the release coat is laminated. The structure of the liner may be formed by pressing the release surface against a tool for transferring structures after the release coat is laminated.

The adhesive layer may be formed from a coating film of an adhesive comprising a self-adherent polymer. A preferable adhesive contains a self-adherent polymer and a crosslinking agent for crosslinking the self-adherent polymer. Herein, the self-adherent polymer means a polymer having tackiness at room temperature (about 25°C). Examples of such a self-adherent polymer include acrylic polymers, polyurethane, polyolefin, polyester, etc.

One example of the synthesis of a self-adherent polymer is explained by making reference to an acrylic polymer.

As a first monomer, an acrylic unsaturated acid (e.g. acrylic acid, methacrylic acid, itaconic acid, maleic acid, etc.) or a polar (meth)acrylic monomer (e.g. acrylonitrile, etc.) is provided. The first monomer is mixed with an acrylic monomer as the second monomer to obtain a monomer mixture. As the second monomer, an alkyl acrylate such as isooctyl acrylate, butyl acrylate, 2-methylbutyl acrylate, 2-ethylhexyl acrylate, isononoyl acrylate, etc. may be used.

The monomer mixture is polymerized by a conventional polymerization method such as solution polymerization, emulsion polymerization, bulk polymerization, etc. to synthesize a self-adherent polymer having a specific molecular weight.

When a crosslinking agent is used to crosslink the self-adherent polymer, the amount of the crosslinking agent is usually from 0.02 to 2 wt. parts, preferably from 0.03 to 1 wt. part, per 100 wt. parts of the self-adherent polymer, although it depends on the kind of the crosslinking agent. Examples of the crosslinking agent include isocyanate compounds, melamine compounds, poly(meth)acrylate compounds, epoxy compounds, amide compounds, bisamide compounds (e.g. bisaziridine derivatives of dibasic acids such as isophthaloyl bis(2-methylaziridine), etc.).

The glass transition temperature (Tg) of the adhesive layer is preferably from -50 to -10°C, particularly preferably from -40 to -5°C. When Tg of the adhesive layer is too high, the adhesion between the adherent and the marking film may deteriorate. When Tg is too low, the adhesive may be squeezed out from the edge of a roll of the marking film, when the marking film is stored in a rolled form, and thus the sticking of the piled parts of the marking film may not be prevented.

Here, Tg of the adhesive layer is calculated from  $\tan \delta$  which is measured using a dynamic viscoelastometer. The measuring conditions include a torsion mode at a shear rate of 1 radian/sec., a heating temperature range of -60 to 100°C, and a heating rate of 5°C/sec. The thickness of the sample is usually from 1 to 2 mm.

The thickness of the adhesive layer is usually from 20 to 100  $\mu\text{m}$ , preferably from 25 to 80  $\mu\text{m}$ . The pressure-sensitive adhesive layer may contain various additives such as tackifiers, elastic microspheres, microspheres of tacky polymers, crystalline polymers, inorganic powders, UV-ray absorbers, etc.

#### PROTECTIVE FILM

The protective film has light transmission properties as a whole. The light transmittance of the protective film is usually at least 60%, preferably at least 70%, particularly preferably at least 80%. Here, the light transmittance is a total light transmittance measured with

a spectrophotometer or a color meter which functions also as a photometer at a wavelength of 550 nm.

The protective film preferably comprises a resin film having a resin with high transparency. Examples of such a resin of the resin film include fluororesins, phthalate base polyesters (e.g. PET, PEN, etc.), acrylic resins, and the petroleum-resistant resins described above, etc. The fluororesin is a polymer obtained by polymerizing at least one fluorine-containing monomer. Examples of the fluorine-containing monomer include fluorine-containing ethylene monomers such as vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene, trifluorochloroethylene, etc. In addition, one or more monomers copolymerizable with the fluorine-containing monomer such as a methacrylate (e.g. methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, etc.) and an acrylate (e.g. methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, etc.) may be mixed with the fluorine-containing monomer(s). The starting monomer may contain other copolymerizable monomer such as an acrylic monomer (e.g. methyl methacrylate, ethyl methacrylate, etc.) in addition to the fluorine-containing monomer. Furthermore, the protective film may be made of a resin composition comprising the fluororesin and the acrylic resin.

When the marking film of the present invention is used as a marking film for a vehicle that moves using a petroleum fuel as an energy source, the resin of the protective film is preferably the fluororesin or the petroleum-resistant resin. In such a case, the percentage of the fluororesin or the petroleum-resistant resin in the resin component constituting the protective film is usually at least 70 % by weight, preferably at least 80 % by weight, particularly preferably at least 90 % by weight. When the protective film contains both the fluororesin and the petroleum-resistant resin, the total amount of the two resins is preferably in the above range.

The thickness of the protective layer is usually from 5 to 120  $\mu\text{m}$ , preferably from 10 to 100  $\mu\text{m}$ . When an adhesive layer is used to adhere the protective film to the receptor film, it has a thickness of usually 20 to 100  $\mu\text{m}$ , preferably 25 to 80  $\mu\text{m}$ .

### FORMATION OF IMAGE

The colorant is usually a toner or an ink. For example, when an image is formed by transferring the toner to the receptor layer, a conventional printing method such as an electrostatic printing method is used to transfer the toner to the back surface of the protective film. The electrostatic printing method includes a direct-print method in which an image is directly printed on the back surface of the protective film and a transfer method in which an image is printed on a temporary support and then is transferred to the protective film. In the transfer method, the image is firstly formed on the temporary support, which may be called a transfer medium, and then transferred to the back surface of the protective film with heating and pressing to obtain the protective layer having the printed image.

The toner used to form the image contains a binder resin and a pigment dispersed in the binder resin. The binder resin may be a resin selected from the group consisting of acrylic resins and polyester resins and a mixture thereof. The details of the electrostatic printing method are disclosed in JP-A-4-216562, JP-A-11-513818, etc.

### Examples

#### Example 1

A receptor sheet in this Example was produced as follows:

A polycarbonate polyurethane and a phenoxy resin were mixed in a weight ratio of 70:30, and then dissolved in toluene to obtain a paint for a receptor layer. The polyurethane was prepared by polymerizing a raw material containing 1,6-hexanediol carbonate polyol and hexamethylene diisocyanate. The phenoxy resin was "PKHH" (trademark ) available from Phenoxy Specialties, USA.

This paint was applied on a polyester carrier (a liner of a polyester film having a thickness of 50  $\mu\text{m}$  with a release layer) to a dry thickness of 10  $\mu\text{m}$ , and then dried to obtain a receptor layer comprising a transparent thermoplastic resin film. The receptor layer (the thermoplastic resin film) had Tg of 24°C. The polyurethane had Tg of 34°C, and the phenoxy resin had Tg of 72°C.

On the back surface of the receptor layer (the surface in contact with the carrier serving as a colorant-receptive surface), a solution of a polyester polyurethane (REZAMIN®



NE310 available from DAINICHI SEIKA Co., Ltd.) was applied to a dry thickness of 33  $\mu\text{m}$  and dried to form a base layer. Thereby, a receptor film consisting of the laminate of the receptor layer and the base layer was obtained.

Separately, a paint for an adhesive layer was applied on a release surface of a liner having a regularly patterned unevenness on the release layer with a knife coater to a dry thickness of 40  $\mu\text{m}$  and dried at 90°C for 5 minutes. This paint was prepared by mixing a self-adhesive acrylic polymer, crystalline polyurethane and a bisamide crosslinking agent in a mixed solvent of ethyl acetate and toluene. A weight ratio of self-adherent polymer: crystalline polyurethane:crosslinking agent was 90:10:0.2 (the ratio of non-volatile components).

The acrylic self-adhesive polymer was a copolymer prepared by solution polymerizing a monomer mixture containing butyl acrylate, acrylonitrile and acrylic acid in a weight ratio of 93:3:4. The self-adherent polymer had a weight average molecular weight of was 460,000 and Tg of -21°C.

The crystalline polyurethane was prepared by polymerizing isophorone diisocyanate (IPDI) and polycaprolactone (PLACSEL® 220 available from DAICEL Chemical Industries, Ltd.; weight average molecular weight = 6,000; weight average molecular weight/number average molecular weight = 1.8) in toluene. The molar ratio of polycaprolactone to IPDI was 2:1. The polyurethane had a weight average molecular weight of 13,000 and a ratio of weight average molecular weight to number average molecular weight of 2.2.

On the release layer of the above liner, a plurality of ridges corresponding to grooves to be transferred to the adhesive layer were continuously formed along the lines of a crosshatch so that the ridges intersected each other. The height of the ridge was 19.5  $\mu\text{m}$ . Thus, the largest depth of the groove on the adhesion surface was 19.5  $\mu\text{m}$ . The maximum distance between the adjacent ridges (the distance between the bottoms of the ridges) was 1.2 mm, and the width of the ridge was 55  $\mu\text{m}$ . The vertical cross section of the ridge was a trapezoid. Correspondingly, the vertical cross section of the groove on the adhesive layer was also a trapezoid.

The adhesive layer with the liner, which was produced in the above, was dry laminated on the back surface of the base layer of the receptor sheet, and then the polyester carrier was removed from the surface of the receptor layer to obtain the receptor sheet of this Example.

Using the receptor sheet obtained, the marking film of this Example was produced as follows:

A digital graphics for transfer was formed on a transfer medium (TRIDENT® manufactured by 3M) with an electrostatic printing system (Scotchprint® 9512 manufactured by 3M). Then, the transfer medium having the printed graphics was rolled in a roll form to obtain a medium roll.

Then, the receptor sheet and the medium roll were set on a laminator (ORCA® III manufactured by 3M), and the laminator was operated under the following conditions, and the toned image was transferred to the receptor sheet to obtain a roll of the marking film of this Example:

Image-transferring conditions

- Temperature of an upper roll: 130°C
- Temperature of a lower roll: 50°C
- Web conveying speed: 70 cm/min.
- Pressure: about 410 kPa (60 psi)

With the marking film of this Example, the image observed through the protective film was clear.

The toner-adhesion test was carried out as follows:

One hundred cross-hatch cuts (size of each section: about 1 mm x about 1 mm) were formed on the toned image, and then an adhesive tape (#610 available from 3M) was adhered to the toned image. The adhesive tape was quickly peeled off. No transfer of the toner to the adhesive tape was observed, which confirmed that the adhesion between the toner and the receptor layer was good.

Separately, a transparent protective film was adhered to the toned image on the marking film (the colorant-receptive surface) with an adhesive to obtain a marking film with a

protective film. The protective film used was a fluororesin-containing protective film with an adhesive layer (Overlamine film SP 4114 available from Sumitomo 3M Ltd.)

The petroleum resistance of the marking film with the protective film was evaluated as follows:

5 Two rectangular pieces of the marking film each having a length of about 50 mm and a width of about 30 mm were provided. One piece was adhered to a stoved melamine coated plate (available from PALTEC) with the adhesive layer of the marking film having the uneven adhesion surface, while the other piece was also adhered to the coated plate with the adhesive layer with overlapping partially with the one piece to obtain a test sample. The overlapped  
10 width of the edges of the pieces in the width direction was about 10 mm. With such overlapping, a petroleum fuel could easily penetrate in a gap between the adhesive layer and the coated plate from the edges of the film so that the test was carried out under relatively severe conditions.

The test sample was fixed so that the longitudinal edge parts with a width of about 10  
15 mm of the two pieces of the marking film were dipped in a diesel oil (available from Mobil Oil Co., Ltd.), and kept standing for 8 hours. Thereafter, the sample was dried in the shade at room temperature for 16 hours, and then its appearance was observed with an eye. At any part of the two pieces of the marking film, no peeling at the interface, no peeling between the layers such as the receptor layer, or no wrinkle was found, and good appearance was  
20 maintained.

The moisture resistance of the marking film was evaluated as described above. No edge of the marking film turned up from the adherent (the stoved melamine coated plate). Thus, the moisture resistance was ranked good.

#### Example 2

25 A receptor sheet in this Example was produced in the same manner as in Example 1 except that a receptor layer was formed from the polycarbonate polyurethane only and a receptor film consisting of such a receptor layer was used. The thickness of the receptor sheet was 33  $\mu\text{m}$ .

With the marking film of this Example, the image observed through the protective film was clear. The adhesion of the toner was good, and no transfer of the toner to the adhesive tape was observed.

5 The petroleum resistance of the marking film was evaluated in the same way as in Example 1. No peeling at the interface, no peeling between the layers such as the receptor layer, or no wrinkle was found, and good appearance was maintained.

The moisture resistance of the marking film was evaluated in the same way as in Example 1. No edge of the marking film turned up.

### Example 3

10 A receptor sheet in this Example was produced in the same manner as in Example 2 except that polycaprolactone polyurethane was used as polyurethane. The polyurethane used in this Example was prepared by polymerizing polycaprolactone, MDI and neopentyl glycol as raw materials. The receptor layer (the thermoplastic resin film) had Tg of 0°C.

15 With the marking film of this Example, the image observed through the protective film was clear. The adhesion of the toner was good, and no transfer of the toner to the adhesive tape was observed.

The petroleum resistance of the marking film was evaluated in the same way as in Example 1. No peeling at the interface, no peeling between the layers such as the receptor layer, or no wrinkle was found, and good appearance was maintained.

20 The moisture resistance of the marking film was evaluated in the same way as in Example 1. No edge of the marking film turned up.

### Example 4

A receptor sheet in this Example was produced in the same manner as in Example 2 except that a receptor sheet was formed from the phenoxy resin only.

25 A roll of a marking film was produced in the same manner as in Example 1 except that the receptor sheet of this Example was used.

With the marking film of this Example, the image observed through the protective film was clear. The adhesion of the toner was good, and no transfer of the toner to the adhesive tape was observed.

The petroleum resistance of the marking film was evaluated in the same way as in Example 1. No peeling at the interface, no peeling between the layers such as the receptor layer, or no wrinkle was found, and good appearance was maintained.

The moisture resistance of the marking film was evaluated in the same way as in Example 1. No edge of the marking film turned up.

#### Comparative Example 1

A marking film of this Comparative Example was produced in the same manner as in Example 2 except that an ionomer film having a thickness of 50  $\mu\text{m}$  (HIMIRAN® 1601 available from MITSUI DUPONT Co., Ltd.) was used as a receptor layer.

With the marking film of this Comparative Example, the image observed through the protective film was clear. The adhesion of the toner was good, and no transfer of the toner to the adhesive tape was observed.

The petroleum resistance of the marking film was evaluated in the same way as in Example 1. The receptor layer was swelled and the marking film was peeled from the adherent.

#### Comparative Example 2

A receptor sheet of this Comparative Example was produced in the same manner as in Example 2 except that a receptor layer was formed from the following polyester polyurethane only.

The polyurethane used in this Comparative Example was prepared by polymerizing a raw material containing 1,6-hexanediol, 1,4-butanediol, adipic acid, IPDI and hydrogenated MDI.

The marking film of this Comparative Example had low toner-transfer properties so that the clearness of the image was lower than those in Examples 1 to 4. When the moisture resistance of the marking film was evaluated in the same way as in Example 1. The edges of the film turned up. Thus, the moisture resistance was apparently inferior to that in Examples 1 to 4.

#### Example 5

A single-layer white film having a thickness of 80  $\mu\text{m}$  was produced from a composition containing a methyl methacrylate (MMA)-butyl acrylate (BA)-methyl acrylate(MA)-styrene (St) copolymer (MMA:BA:MA:St = 69:23:3:5 by weight) and titanium oxide, and used as a receptor layer. The receptor layer had a glass transition temperature  $T_g$  of 56°C.

The film was cut to a width of 25 mm, and its elongation was measured using a Tensilon tester at 20°C, a clamping distance of 100 mm and a pulling rate of 300 mm/min. The elongation was 55%.

Separately, in the same manner as in Example 1, the paint for an adhesive layer was applied to a release surface of a liner and dried to obtain an adhesive layer having a liner. Then, the receptor layer film produced in the previous step was dry laminated to the adhesive layer to obtain a receptor sheet of this Example.

A digital graphics for transfer was formed in the same manner as in Example 1. Then, the toned graphics was transferred to the above receptor sheet under the same conditions as those applied in Example 1 except that the upper roll temperature was 135°C to obtain the marking film of this Example. The paper carrier of TRIDENT® was peeled off. The visual observation confirmed that the toned image had completely been transferred.

The toner-adhesion test was carried out in the same manner as in Example 1. No transfer of the toner to the adhesive tape was observed, which confirmed that the adhesion between the toner and the receptor layer was good.

Separately, the same transparent protective film as that used in Example 1 was adhered to the toned image on the marking film (the colorant-receptive surface) with the adhesive to obtain a marking film with a protective film.

The petroleum resistance of the marking film with the protective film was evaluated as follows:

The marking film was cut to obtain a 50 mm square piece, and adhered to a stoved melamine coated plate (available from PALTEC) with the adhesive layer of the marking film to obtain a test sample. The sample obtained was fixed so that the lower edge of a width of about 10 mm of the marking film was dipped in a diesel oil (available from Mobil Oil Co.,

Ltd.), and kept standing for 8 hours. Thereafter, the sample was dried in the shade at room temperature for 16 hours, and then its appearance was observed with an eye. At any part of the marking film, neither swelling nor peeling of the film was observed, and good appearance was maintained.

5     Comparative Example 3

          A receptor sheet in this Comparative Example was produced in the same manner as in Example 5 except that a polymethyl methacrylate film having a thickness of 80  $\mu\text{m}$  was used in place of the MMA-BA-MA-St copolymer. The elongation of this polymethyl methacrylate film was 5% when measured under the same condition as those in Example 5. This  
10     elongation means that this film had little elongation, so that followability to curved surfaces was insufficient for use in a marking film.

          A marking film was produced in the same manner as in Example 5 except that the receptor sheet obtained in the above step was used. However, a part of the toner remained on the paper carrier and thus the transferability of the toner was unsatisfactory. Nevertheless, the  
15     once transferred toner did not transfer to the adhesive tape in the toner-adhesion test, and had good adhesion properties.

          In the same manner as in Example 5, a protective film was adhered to the toned image of the marking film to obtain a marking film with a protective film, which was subjected to the petroleum resistance test. Neither swelling nor peeling of the film was observed.

20     Comparative Example 4

          A receptor sheet in this Comparative Example was produced in the same manner as in Example 5 except that an acrylic resin film having a thickness of 50  $\mu\text{m}$  which comprised BA (90 parts by weight) and acrylic acid (10 parts by weight) was used in place of the MMA-BA-MA-St copolymer. This film had a Tg of  $-50^{\circ}\text{C}$ . The surface of this film had tackiness and  
25     thus it was not suitable for use as a receptor layer of a marking film.